



## Developmental Studies on Novel Biodegradable Polyester Films from Maravetti Oil

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### Abstract

Novel biodegradable polyester film was synthesised from naturally available Maravetti oil, formic acid and 30% hydrogen peroxide by stepwise polymerisation technique. The polymer was prepared by resin react with styrene. The UV, FTIR and NMR spectral studies carried out to identify the nature of the polymer formed. SEM analysis confirmed that the polymer was biodegradable in nature. The biodegradability of the polyester film was studied by soil burial test. The thermal degradation at different time intervals were analysed by TG-DTA analysis. The cross-linking ability of the polymers was checked by DSC analysis. Mechanical properties like tensile strength and impact strength were characterized. The resulted polymers have satisfied mechanical performance and fast curing speed.

**Keywords:** Cross-linking; Degradation; Polymer Soil Burial; Styrene.

### 1. INTRODUCTION

In our world over 6.3 billion plastics are generated, only 9% is recycled, 12% incinerated, 79% accumulated in natural environment. In the production of plastics, monomers used which are derived from fossil hydrocarbons. Most of the plastics are slow to degrade (Roland Geyer *et al.* 2017). Because of increasing prize of petroleum and environmental awareness, researchers are interested in the synthesising of polymers from renewable resources of plants. Plant oils are considered building blocks of polymers due to their low cost, availability and eco-friendly (Barnes *et al.* 2009). Active functional groups such as double bonds, ester groups and hydroxyl groups, on the triglyceride chain make the polymer to be chemically modified and to synthesis polymers with desirable properties (Wang *et al.* 2008). Hydnocarpus Wightiana seed oil or chaulmoogra oil also known as Maravetti oil. It has been used in medicine as antibiotics for the treatment of several skin diseases and leprosy as a mixture suspended in gum or as an emulsion (Nortan, 1994). The oil is unusual in not being made up of straight chain fatty acids but acids with a cyclic group at the end of the chain.

### 2. EXPERIMENTAL METHODS

#### 2.1 Materials

Maravetti oil (MVO) was purchased from local market, Formic acid (97%) (Rankem), Hydrogen

peroxide (30%) (Rankem) were used in the first step functionalization. Maleic acid (Rankem) and Morpholine (Rankem). Benzoyl peroxide (Rankem) was used as a radical initiator and N, N-Dimethyl aniline (Rankem) was used as accelerator in the curing process. Styrene (Rankem) was used as a vinyl co monomer.

#### 2.2 Synthesis of Maravetti Oil Polyol

100 g of maravetti oil was taken in a three necked flask fitted with condenser and thermometer. 100 ml of 97% formic acid and 55 ml of 30% hydrogen peroxide was added and the reaction mixture was vigorously stirred over 16h. Ice water bath was used externally to keep the temperature below 40°C. The resulting emulsion was poured into a separating funnel and extracted with ether. The ether layer was dried over anhydrous sodium sulphate and the resulting product was polyol resin from Maravetti oil.

#### 2.3 Synthesis of Polyesters

The polyol resin was heated in a three necked flask and maleic anhydride was added in 1:2 ratio at 70 °C. Morpholine was used as a catalyst. After 2 hours a golden yellow viscous liquid formed it indicates the formation of oligomerised maravetti oil fumarate resin.

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## 2.4 Synthesis of Polyester Film from Oligomerised Maravetti Oil Fumarate Resin and Co-Monomer Styrene

Synthesis of aliphatic polyester was carried out by free radical addition polymerisation reaction by using the homopolymer (oligomerised maravetti oil fumarate resin) and styrene at different concentration using benzoyl peroxide as catalyst and Dimethyl aniline as accelerator. The viscous liquid is transferred in to glass mould coated with silicon oil at room temperature. The polyester thin film of different concentration such as 1:0.5, 1:1 and 1:2 were synthesised from homo polymer and styrene. Finally the yellow coloured polyesters sheets were removed from the mould.

## 2.5 Characterisation of Resins

The UV and FTIR analysis were carried out for maravetti oil, hydroxylated maravetti oil and also the resin. The  $^1\text{H-NMR}$  spectra for epoxy resin, polyols

and pre-polymers were dissolved in  $\text{CDCl}_3$  and recorded using BRUKER AVANCE III, 400 MHz FT NMR SPECTROPHOTOMETER. Cured samples were also checked to see the degree of curing. The Thermo Gravimetric Analysis (TGA) was done by using TGA instrument. The Differential Scanning Calorimetry (DSC) analysis was done by a TA instrument.

## 3. RESULT & DISCUSSION

### 3.1 FTIR Analysis

The FTIR spectra of maravetti oil, Hydroxylated maravetti oil and the resins were recorded between  $500\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  (Rohan *et al.* 2018). In hydroxylated MVO, the FTIR spectra showed a strong absorption band at  $3522.74\text{ cm}^{-1}$ , due to the presence of free-OH group in the molecule, which is absent in MVO. A strong absorbance band in  $1734.85\text{ cm}^{-1}$  is due to the presence of C=O in esters. A strong band in  $2926.78\text{ cm}^{-1}$  due to the symmetrical-C-H bond in  $-\text{CH}_2-$  group of the side chain.

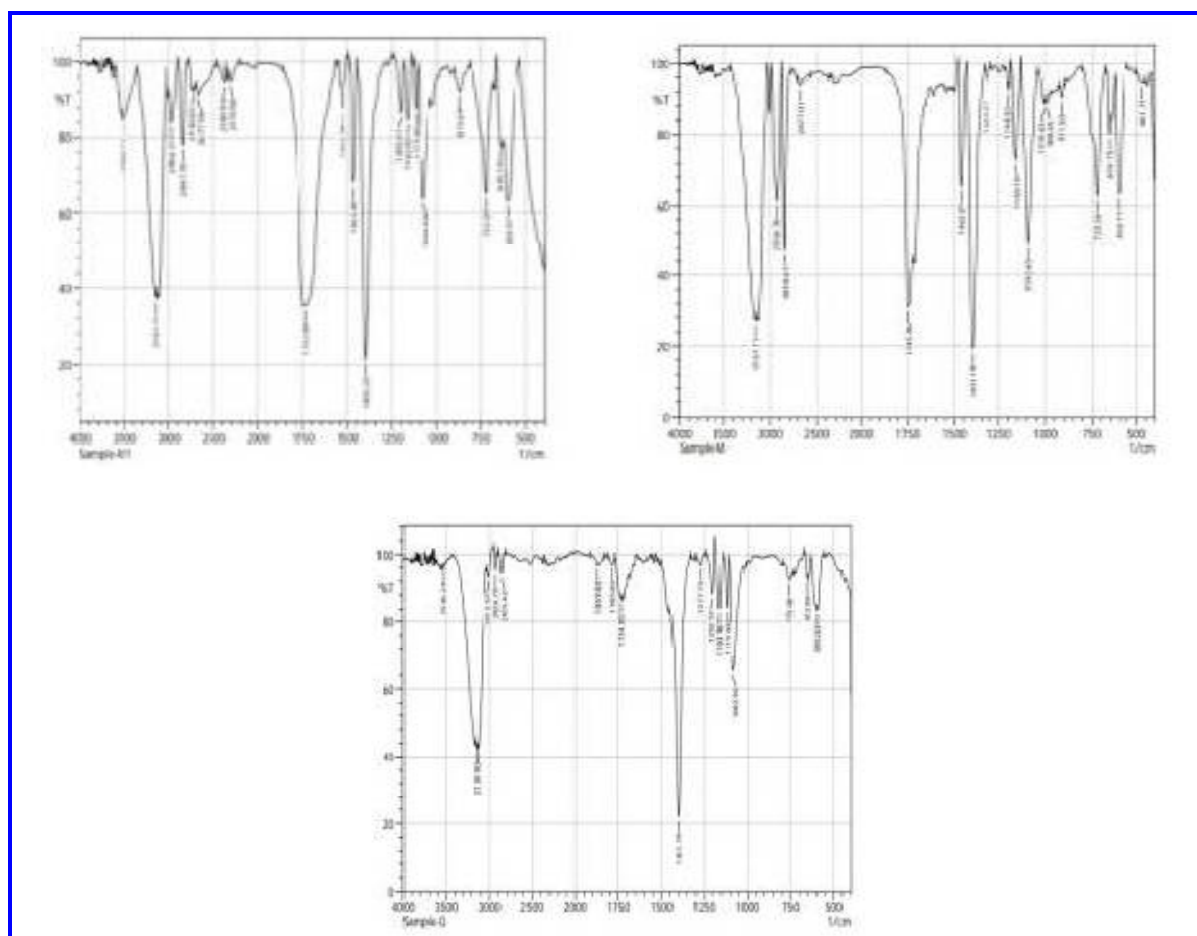


Fig. 1: IR spectra of MVO, Hydroxylated MVO and MVO Resin

Table 1. FT-IR probable assignment

| Probable assignment                                 | MVO (cm <sup>-1</sup> ) | Hydroxylated MVO (cm <sup>-1</sup> ) | MVO Resin (cm <sup>-1</sup> ) |
|---|-------------------------|--------------------------------------|-------------------------------|
| -CH <sub>2</sub> Group                              | 2926.78                 | 2966.31                              | 2926.78                       |
| -C- O Group in GM                                   | 2848.67                 | 2847.7                               | -                             |
| C=O in esters                                       | 1745.46                 | 1733.89                              | 1734.85                       |
| Terminal CH <sub>3</sub> Groups                     | 1194.82                 | 1200.61                              | 1202.53                       |
| Carboxyl Group of acids                             | 1160.10                 | 1163                                 | 1163.96                       |
| -CH-CH- Stretching                                  | 1092.60                 | 1084.88                              | 1082.96                       |
| CH <sub>2</sub> - sequences of the aliphatic chains | 720.36                  | 722.29                               | 755.08                        |
| -OH Group   | 3161.11                 | 3522.74                              | 3536.24                       |

### 3.2 UV Analysis

The UV spectra of the oil, hydroxylated triglyceride oil and for the resins have been investigated (220 nm - 800 nm). The oil sample showed an electronic absorption band around 239 nm. The hydroxylated oil exhibited a blue shift when compared with the corresponding parent oil which is attributed to the substitution of hydroxyl group at the unsaturated moiety. There is also decrease in the absorbance in comparison with that of parent oil is due to the substitution of the hydroxyl group at the olefinic double bond and also distortion of geometry. The substantial red shift in electronic absorption exhibited in the resin due to the substitution of the fumarate group and also due to the distortion in geometry of the molecule by the introduction of fumarate group (Priya Rajini and Begila David, 2015).

### 3.3 <sup>1</sup>H NMR spectral studies

The <sup>1</sup>H NMR spectra recorded from resin of MVO are shown in Fig 3. The peaks in <sup>1</sup>H NMR for quantitating unsaturated fatty acids are those of the terminal methyl protons (0.86-0.88 ppm), olefinic protons (5.3-5.6 ppm), methylene -CH<sub>2</sub>- (1.2-1.6 ppm) protons attached to allylic carbon (2.00-2.04 ppm) and protons attached to the bis-allylic carbons (2.2 - 2.6 ppm). The corresponding olefinic protons peak in the hydrolysis product has almost disappeared, showing the double bonds in oil is replaced by the hydroxyl group. This peak is shifted to 8.0 ppm in the MVO resin due to

the deshielding effect of hydroxyl and carboxylate ester linkages (Shakina *et al.* 2011).

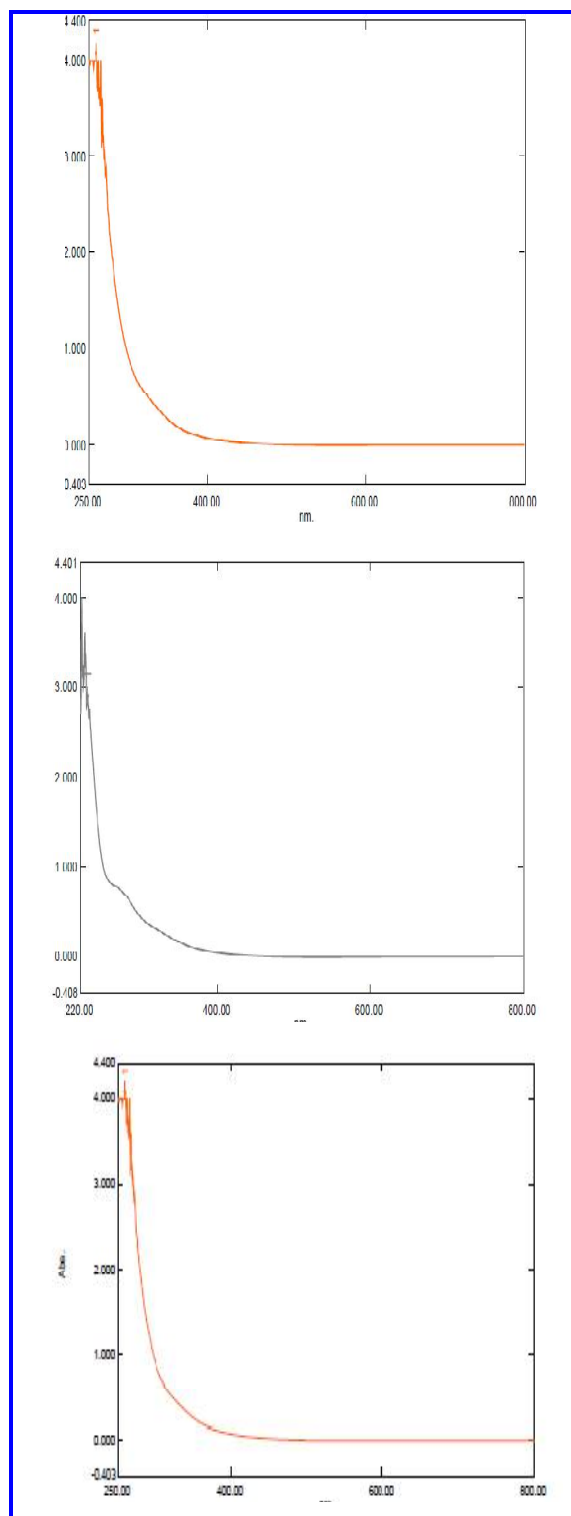


Fig. 2: UV spectra of MVO, Hydroxylated MVO and MVO Resin

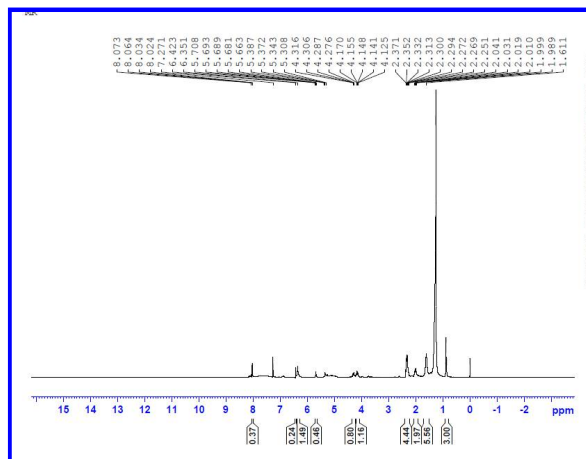


Fig. 3: NMR Spectrum of MVO Resin

### 3.4 XRD Pattern of Polymer Composite

From XRD analysis, average crystallite size is 7.02 nm. Peak is narrow, hence the polymer composite is crystalline (Birendra Pratap Singh *et al.* 2012).

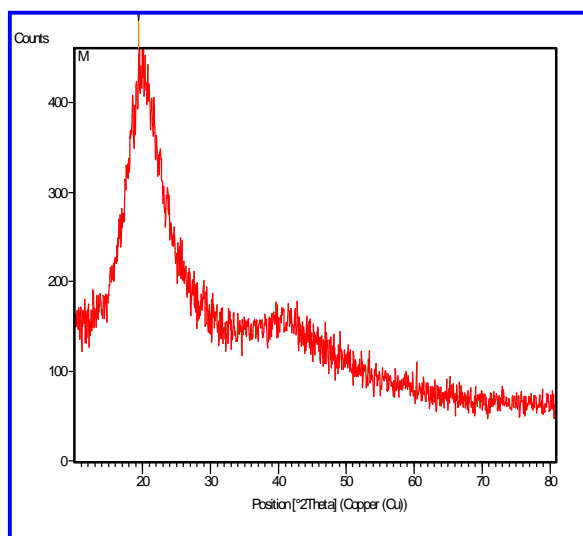


Fig. 4: XRD pattern of MV polymer

### 3.5 Thermal Analysis

Properties of polymer affected by the cross linking degree, which correlated with the degree of functionality of the monomer. DSC can be used to check the curing results of the thermosetting resin. Both the resins with cross linker and without cross linker were analysed by DSC. The peak for the sample with cross linker is 527.19 °C, indicating the fastest cure for this resin will occur at the temperature. The onset of the cure peak for this resin is 412.00 °C and the total heat of the reaction is 3853J/g (Li *et al.* 2017).

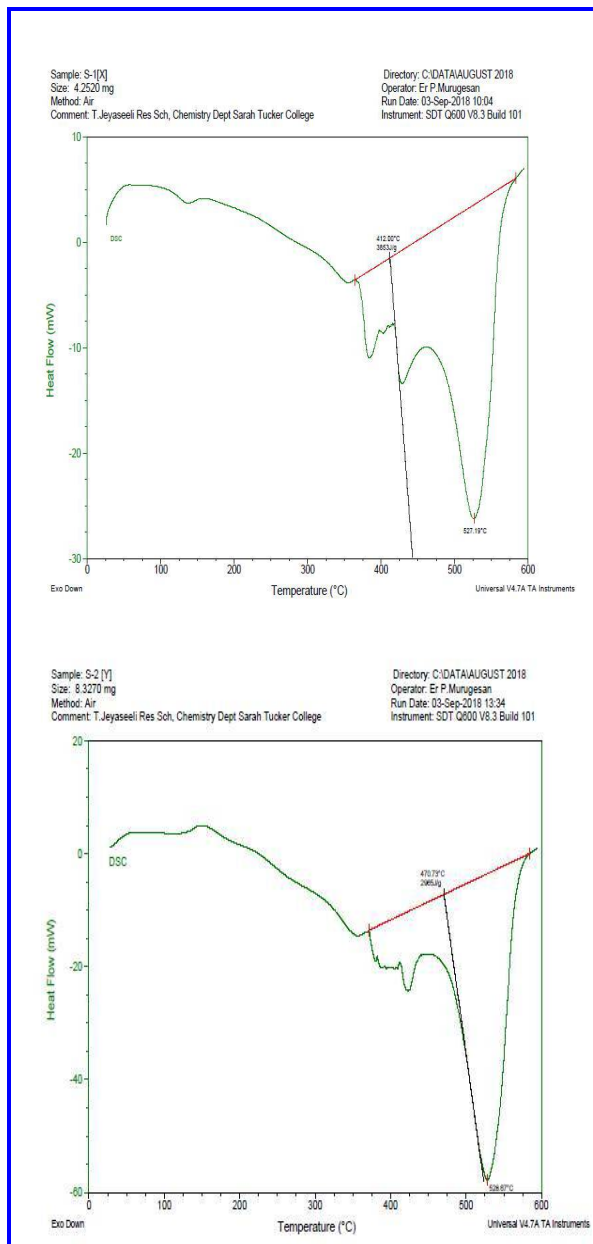
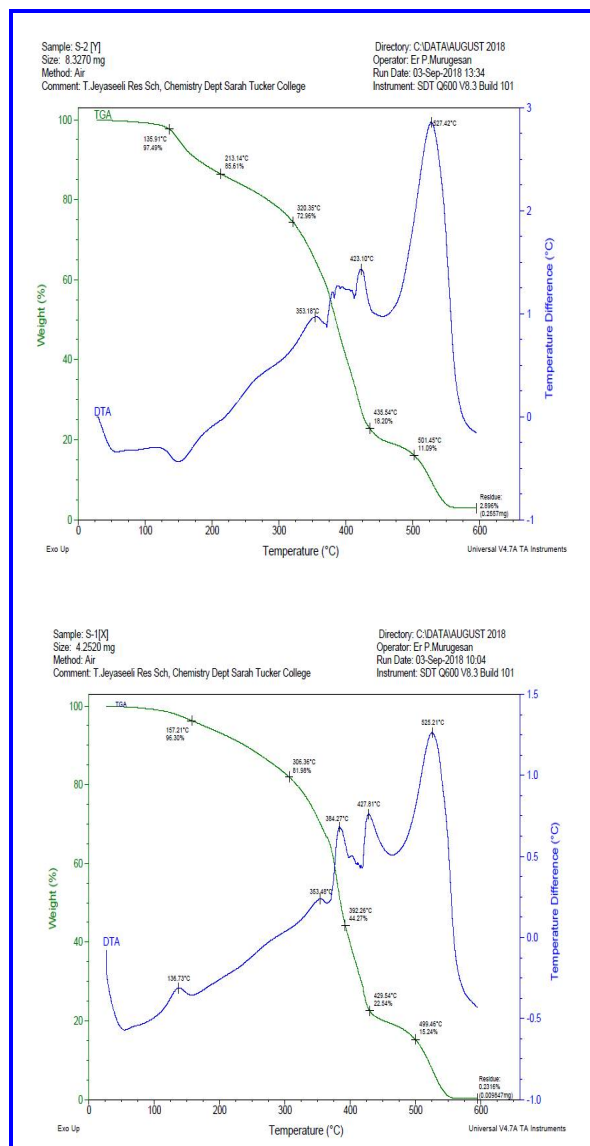


Fig. 5: DSC thermograms of polymer composite and without cross linker

The peak for the sample without cross linker is 528.6 °C, indicating the fastest cure for this resin will occur at the temperature. The onset of the cure peak for this resin is 470.73 °C and the total heat of the reaction is 2965J/g. It can be seen that resins with cross linker released out more heat during the curing process, which indicate more double bonds inside the resins. TGA for resins was conducted to identify their degradation characteristics.



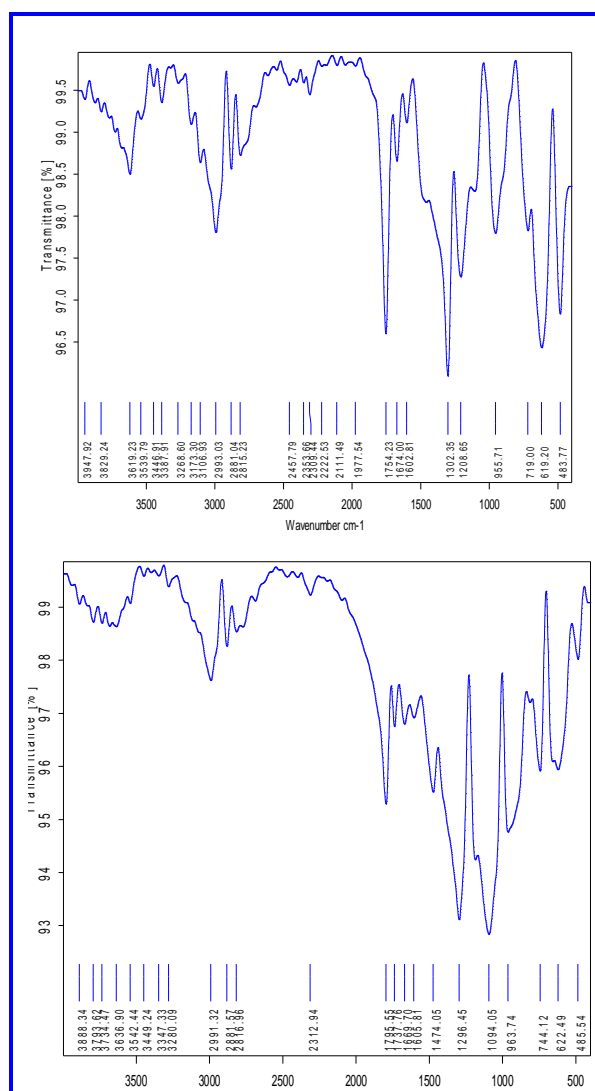
**Fig. 6: TGA, DTA thermograms of sample with and without cross linker**

The resin with cross linker was stable up to 150 °C with no significant weight loss, the initial weight loss was observed at 157.21 °C, indicating the loss of volatiles and moistures. Significant weight loss began at 306.36 °C due to the degradation of the resin. When the temperature reached 499.46 °C, weight loss was recorded. The maximum rate of decomposition occurred at 525.21 °C; the residual mass is around 0.009847 mg. The resin without cross linker was stable upto 130 °C with no significant weight loss; the initial weight loss was observed at 135.91 °C, indicating the loss of volatiles and moistures. Significant weight loss began at 320.35 °C due to the degradation of the resin. When the temperature reached 510.45 °C, weight loss

was recorded. The maximum rate of decomposition occurred at 527.42 °C; the residual mass is around 0.2557 mg. From this, we see that for resins with cross linker are more resistive to temperature increasing, this is due to cross linker increased the cross linking network of the resins. The residue percentage is lower than resins without cross linker (Sathish Kumar *et al.* ).

### 3.6 FTIR-ATR Analysis

The samples were analysed over the range of 4000 $\text{cm}^{-1}$  - 400 $\text{cm}^{-1}$  with a spectrum resolution of 4  $\text{cm}^{-1}$ . All spectra were averaged over 64 scans. The cross linking was confirmed through the ATR spectral studies.



**Fig. 7: ATR Spectrum of polymer composite with and without cross linker**



The strong peaks observed at  $1737.76\text{ cm}^{-1}$  and  $1754.23\text{ cm}^{-1}$  indicate that the surface of the sample with and without cross linker are comprised predominantly with ester linkages (Shakina *et al.* 2014).

### 3.7 SEM Analysis

SEM micrographs show the strong bonding in composite without cross linker than in with cross linker. These results clearly provide strong interfacial adhesion and good wetting, as evidenced by the almost complete absence of holes around the matrix and paucity of breaking of bio-flour during tensile fracture (Prabha Littis Malar and Begila David, 2015).

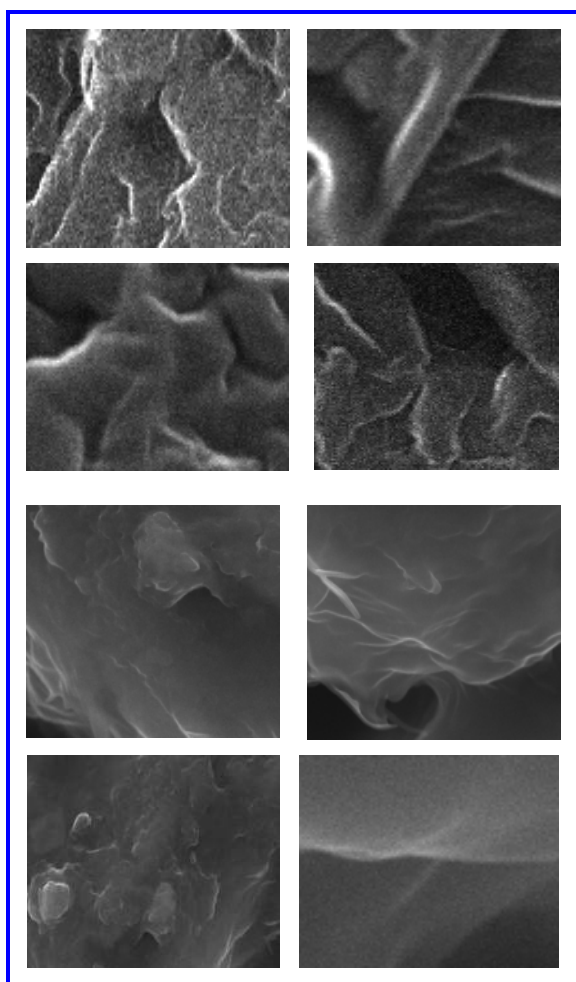


Fig. 8: SEM Photographs of polymer composite with and without cross linker

### 3.8 Microbial Studies

Antibacterial present in the sample were detected by Agar well diffusion method using bacterial

strains *Actinomycetes Israelii* and *Aeromonas hydrophilla*. The newly prepared biopolyesters showed potential antibacterial activity against micro organisms. Antifungal present in the sample was detected by Agar well diffusion method using fungal strain *Aspergillus Niger*. The newly prepared biopolyesters showed potential antifungal activity against micro organisms (Shakina *et al.* 2012).

## 4. CONCLUSION

We have synthesized Bio-based thermoset resin from *Hydnocarpus wightiana* seed oil fatty acid. It was hydroxylated by hydrogen peroxide and formic acid; the resulted resin was modified by maleic anhydride. The obtained resins were used in the preparation of the bio based composites. The composites were characterised by different mechanical analysis and showed relatively good flexural and impact strength which is comparable with the glass fibre reinforced composites.

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